I. A NEW SYNTHETIC ROUTE TO UNSATURATED ALKANOLAMINES

II. THE SYNTHESIS OF SUBSTITUTED DIBENZYLTROPOLONES

BY

JAMES WESLEY BERRY

B.A., Augustana College, 1949

R. UNIV. BIBLIOTHEEK LEIDEN

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1953

URBANA, ILLINOIS
1953

I. A NEW SYNTHETIC ROUTE TO UNSATURATED ALKANOLAMINES

II. THE SYNTHESIS OF SUBSTITUTED DIBENZYLTROPOLONES

BY

JAMES WESLEY BERRY

B.A., Augustana College, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1953

URBANA, ILLINOIS
1953

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Nelson J. Leonard for suggesting this research, and for his encouragement and assistance during its course.

He is indebted to Miss Elizabeth Petersen, Miss Helen Miklas, Mrs. Robert Hill, and Mrs. Bruce Burnett for the infrared and ultraviolet spectra.

The author also wishes to thank the Graduate College for a fellowship held during the fall semester, 1952-1953.

PART ONE

A NEW SYNTHETIC ROUTE TO UNSATURATED ALKANOLAMINES

Introduction

The synthesis of 1-hydroxymethylcycloalkenes by the reduction of β-ketoesters with lithium aluminum hydride has been reported by Dreiding and Hartman (1). This method suggested a new synthetic route to unsaturated alkanolamines in the 1,2,5,6-tetrahydropyridine, Δ^3-pyrroline, and 1,2-dehydropyrrolizidine systems. Physiological activity in certain esters of 1-ethyl-3-hydroxymethyl-1,2,5,6-tetrahydropyridine seemed probable, in view of the structural similarity between this alkanolamine and tropine, the alkanolamine moiety of atropine.

Discussion of Results

A new synthetic route to unsaturated alkanolamines has been found: the reduction of five-and six-membered cyclic amino β-ketoesters with lithium aluminum hydride. Specifically, the synthesis of 1-ethyl-3-hydroxymethyl-1,2,5,6-tetrahydropyridine and certain of its esters, and of 1-*n*-butyl-3-hydroxymethyl-Δ^3-pyrroline has been accomplished. The level of antispasmodic activity of 1-ethyl-1,2,5,6-tetrahydropyridylmethyl diphenylacetate hydrochloride was found to be about one-third that of atropine sulfate.

BIBLIOGRAPHY

1. A. S. Dreiding and J. A. Hartman, Abstracts of Papers, 118th Meeting, American Chemical Society, Sept. 3, 1950, p. 38N.

PART TWO

THE SYNTHESIS OF SUBSTITUTED DIBENZYLTROPOLONES

Introduction

Leonard and Robinson have accomplished the synethesis of 3,7-dibenzyltropolone by the isomerization of 3,7-dibenzylidene-1,2-cycloheptanedione with hydrogen bromide in acetic acid (1).

The fact that the aromatization of 2,6-dibenzylidenecyclohexanone to 2,6-dibenzylphenol has been accomplished with palladium catalysts (2), as well as with hydrogen bromide in acetic acid (3), suggested that substituted dibenzyltropolones might be obtained by aromatiza-

tion of the corresponding 3,7-dibenzylidene-1,2-cycloheptanediones with palladium charcoal catalyst.

Discussion of Results

Substituted 3,7-dibenzyltropolones have been synthesized by the aromatization of certain 3,7-dibenzylidene-1,2-cycloheptanediones with palladium charcoal catalyst and with hydrogen bromide-acetic acid. In particular, 3,7-dibenzyltropolone, 3,7-di(*p*-methylbenzyl)tropolone, 3,7--di(*p*-methoxybenzyl)tropolone, 3,7-di(*o*-chlorobenzyl) tropolone, and 3,7-di(*p*-nitrobenzyl)tropolone were obtained by the aromatization of the correspondingly substituted 3,7-dibenzylidene-1,2-cycloheptanediones with palladium charcoal catalyst. Aromatization with hydrogen bromide-acetic acid was found applicable to the synthesis of those tropolones which did not contain ether groups. The infrared and ultraviolet absorption spectra of these compounds resembled closely the spectra of tropolones of established structure.

The ultraviolet absorption spectra of substituted α,α'-dibenzylidenecycloheptanones and α,α'-dibenzylidene-1,2-cycloheptanediones were determined. They were found to be similar to the spectra of substituted chalcones, in that the shifts caused by introduction of a series of similar substituents into the benzene rings in each series are practically identical throughout.

BIBLIOGRAPHY

1. N. J. Leonard and G. C. Robinson, J. Am. Chem. Soc., **75**, 0000 (1953).
2. E. Horning, J. Org. Chem. **10**, 263 (1945).
3. R. Weiss and J. Ebert, Monatsh. **65**, 399 (1935).

VITA

The author was born on March 23, 1926, in Rankin, Illinois. He received his primary and secondary education in the public schools of Chatsworth, Illinois and Rock Island, Illinois. After serving in the United States Army during 1944-1945, he enrolled at Augustana College in Rock Island, Illinois and received the Bachelor of Arts degree in 1949. The author entered the Graduate College of the University of Illinois in September, 1949. During the school years of 1949-1950 and 1950-1951, he held a teaching assistantship, and during 1951-1952 he held a duPont research assistantship. The author was employed as a research assistant for the Government Rubber Program at the University of Illinois during the summers of 1950, 1951, and 1952. During the fall semester of 1952-1953 he held a University Fellowship. He is a member of Sigma Xi and Phi Lambda Upsilon.